

Fitting by Orthonormal Polynomials of Silver Nanoparticles Spectroscopic Data

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Abstract. Our original Orthonormal Polynomial Expansion Method (OPEM) in one-dimensional version is applied for first time to describe the silver nanoparticles (NPs) spectroscopic data. The weights for approximation include experimental errors in variables. In this way we construct orthonormal polynomial expansion for approximating the curve on a non equidistant point grid. The corridors of given data and criteria define the optimal behavior of searched curve. The most important subinterval of spectra data is investigated, where the minimum (surface plasmon resonance absorption) is looking for. This study describes the Ag nanoparticles produced by laser approach in a ZnO medium forming a AgNPs/ZnO nanocomposite heterostructure.

1 Introduction

The metal nanostructures have attracted considerable attention due to their optical properties. It is related to the efficient excitation of collective electron oscillations, plasmons, which define the particle response to external electromagnetic field. For some metals, as silver, the plasmon resonance is realized in the near UV or visible spectral range. This makes the metals good candidates for resonance plasmon excitation [1]. These properties of metal nanoparticles are used in techniques for applications in optical, electronic, catalytic, sensing and biomedical devices [2–5]. The laser annealing leads to decomposition of the layer into nanoparticles by a dewetting mechanism [2]. The evolution of the dewetting process is a function of a thin film composition and dictates a size distribution and spacing of the nanoparticles. The properties of nanostructures of noble metals are strictly related to a material in which they are embedded. The NPs incorporation into dielectric or semiconductor matrices can lead to emergence of new features of composite materials showing properties different from those of individual components [3–5]. The application of methods for precise study of the resonance absorption band position of noble metal nanoparticles is of a particular interest.

2 Physical data

The silver nanoparticles are produced by pulsed laser deposition (PLD) on quartz substrates SiO₂ (001) in a vacuum chamber. The films are deposited by a laser of type Nd:YAG ($\lambda = 355$ nm,

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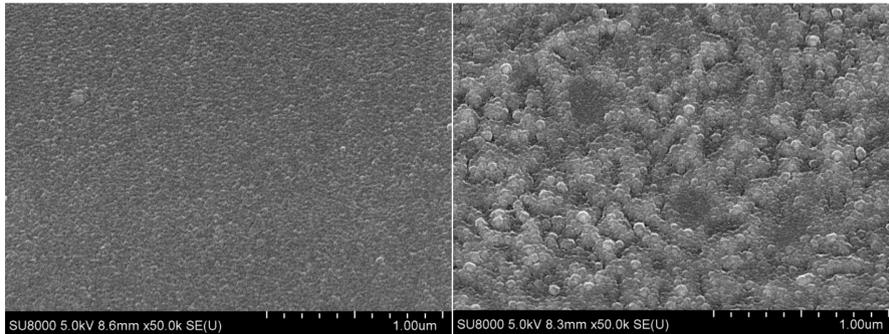


Figure 1. SEM images of Ag/ZnO before (left) and after the laser nanostructuring

$\tau = 18$ ns, $\nu=10$ Hz) at fluence of $F = 1.5$ J/cm² at room temperature. The films are post-deposition annealed for surface nanostructuring by laser-induced decomposition of the film into nanoparticles with diameters of **few tens of nanometers**. The deposited films are laser annealed in air by the same laser system with a fluence of 200 mJ/cm². **The transmission T** of the Ag nanoparticles as a function of **wavelength λ** is analyzed using a UV-VIS spectrometer (HR 4000 Ocean optics) in the range of 220–800 nm. We have chosen one subinterval with $M = 94$ points and λ in [468.9,493.2] and the smaller one with λ in [468.9,481.7]. The selected curve corresponds to the transmission spectrum of AgNPs after the annealing by 10 laser pulses. The lower number of pulses leads to incomplete decomposition of the layer into nanoparticles. The Ag nanoparticles with a mean size of 30 nm are described here. The PLD grown thin film is transformed into a discontinuous structure of small particles. Changes in the resonance absorption are associated with changes in size, shape and interparticle distances, as well as with the dielectric constant of the surrounded medium [3–5].

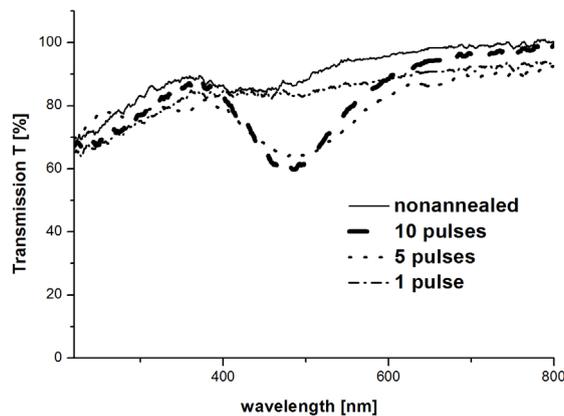


Figure 2. Transmission spectrum of Ag/ZnO nanocomposites before and after the laser annealing

The problem is to find a position of a plasmon resonance. For this aim we have to define a minimum of transmission curve. The mathematical task is to find the best fitting curve and its minimum.

3 Mathematical approach

One defines a new variance at the i -th given point $(\lambda_i, T_i, \sigma_{T_i}, \sigma_{\lambda_i})$, $i = 1, 2, \dots, M$, following [6]: $S_i^2 = \sigma_{T_i}^2 + (\partial T_i / \partial \lambda_i)^2 \sigma_{\lambda_i}^2$. Here we use the Bevington's (1969) proposal to combine both variable uncertainties and assign them to dependent one. **The generalized OPEM [7]:** Our principal relation

for one-dimensional generation of orthonormal polynomials by Forsythe [8] $\{P_i^{(0)}, i = 1, 2, \dots\}$ and their derivatives $\{P_i^{(m)}, m = 1, 2, \dots\}$ in an **arbitrary** discrete set in M points is as follows:

$$P_{i+1}^{(m)}(\lambda) = 1/\nu_{i+1} \left[(T - \mu_{i+1})P_i^{(m)}(\lambda) - (1 - \delta_{i0})\nu_i P_{i-1}^{(m)}(\lambda) + mP_i^{(m-1)}(\lambda) \right]. \quad (1)$$

The generalization of Forsythe procedure in one-dimensional case is with involving arbitrary weights in every points, evaluating derivatives ($m > 0$) or integrals ($m < 0$) and normalizing polynomials. Here the normalization coefficient $1/\nu_i$ and the recurrence coefficients μ_i, ν_i are given as scalar products of the polynomials in the given data in M points in our paper [9]. We developed some features of our algorithm. One can generate $P_i^{(m)}(\lambda)$ recursively. The polynomials satisfy the following orthonormality relations $\sum_{i=1}^M w_i P_k^{(0)}(\lambda_i) P_l^{(0)}(\lambda_i) = \delta_{k,l}$ over the discrete point set $\{\lambda_i, i = 1, 2, \dots\}$, where $w_i = 1/(\sigma_{T_i}^2)$ are the corresponding weights. An approximation function T^{appr} is constructed with orthonormal a_k and usual c_k coefficients. The coefficient matrix in the least square method becomes an identity one, and the coefficients a_k are computed by known values $\{P_k, \lambda_k, w_i\}$ due to orthonormality:

$$T^{\text{appr}(m)}(\lambda) = \sum_{k=0}^L a_k P_k^{(m)}(\lambda) = \sum_{k=0}^L c_k \lambda^k, \quad \text{where} \quad a_k = \sum_{i=1}^M T_i w_i P_k^{(m)}(\lambda_i). \quad (2)$$

Let us write polynomials in the ordinary basis (see [10])

$$P_k = \sum_{j=0}^k c_j^{(k)} \lambda^j, \quad k = 0, \dots, L, \quad \text{then} \quad c_j = \sum_{i=j}^L a_i c_j^{(i)}, \quad j = 0, \dots, L \quad (3)$$

The knowledge of a_i enables to calculate c_j from Eq. (3). The inherited errors in usual coefficients are given by the inherited errors in orthonormal ones:

$$\Delta c_j = \sqrt{\sum_{i=j}^L (c_j^{(i)})^2} \Delta a_i, \quad j = 0, 1, 2, \dots, L, \quad \text{where} \quad \Delta a_i = \sqrt{\sum_{k=1}^M P_i^2(\lambda_k) w_k (T_k - T_k^{\text{appr}})^2}, \quad i = 0, \dots, L.$$

The OPEM advantages are: a) We use unchanged the coefficients of the lower-order polynomials to calculate the higher ones. In this way we shorten the computing time. b) We avoid the inversion of the coefficient matrix to obtain the solution [9–11]. c) We define two criteria for evaluating of an optimal polynomial degree.

First criterion (i): Here one neglects the errors in λ variable, the graph of the fitting curve lies inside the “old” error corridor $[T - \sigma, T + \sigma]$. (ii): After calculating the derivatives at any point λ_i using Eqs. (1), (2), (3) the fitting curve has to lie inside the total error corridor $[T - S, T + S]$.

Second criterion We extend the above algorithm to include S_i^2 in OPEM in two stages: (i): By minimizing the following $\chi^2 = \sum_{i=1}^M w_i [T^{\text{appr}}(\lambda_i) - T(\lambda_i)]^2 / (M - L - 1)$, with weights $w_i = 1/\sigma_{T_i}^2$; (ii): The next approximation is done with the weight function $w_i = 1/S_i^2$. The preference is given to the first criterion and when it is satisfied, the search for the minimal χ^2 stops. Based on the above features the OPEM selects the optimal solution for a given set $\{T, \lambda\}$.

4 Approximation results

The main results are given in Table 1. and Fig. 3. We use one subinterval with $M = 94$ points around a supposed minimum of T and other subinterval with $M = 50$ points in it. We present the approximation with orthonormal coefficients. There are two different type of weights. The table shows: number of

Table 1. OPEM approximations results for different given subintervals

M	L	$\sqrt{\chi^2}$	W	$\Delta T_{\max}[\%]$	$\lambda(\Delta T_{\max})$ [nm]	$T_{\min}^{\text{appr}}[\%]$	$\lambda(T_{\min}^{\text{appr}})$ [nm]
50	2	0.12	$10^3/T^2$	0.57	481.7	59.67	481.7
94	2	0.27	$10^3/T^2$	0.84	474.9	60.32	481.9
94	3	0.23	1.	0.73	493.2	59.85	485.6

points M , optimal number of degrees of polynomials L , $\sqrt{\chi^2}$, maximal deviation between the given and the fitted values $\Delta T_{\max} = \max |T^{\text{appr}} - T|$, λ [nm] at ΔT_{\max} , and the interesting results: T_{\min}^{appr} and the corresponding $\lambda(T_{\min}^{\text{appr}})$. The best results by the given criteria are: in the second row with $T_{\min}^{\text{appr}} = 60.32$, in 481.9 nm at $L = 2$ and in the third row with $T_{\min}^{\text{appr}} = 59.85$, in 485.6 nm at $L = 3$.

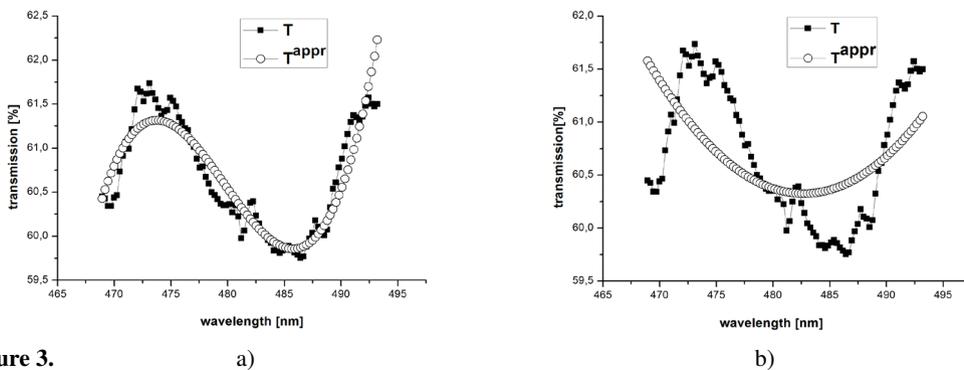


Figure 3.

Given and OPEM approximated values of T by the third a) and the second b) order of polynomials (Table 1).

5 Main Conclusions

The results in Table 1. and Fig. 3. present smooth approximations by the second and the third number of degrees of polynomials in non-equidistant grid and show the minimums by two approaches. The OPEM gives numerical estimations for interpretations of the optical properties of laser produced NPs.

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